VCM PROCESS DESIGN
An ABET 2000 Fully Compliant Project

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Process design projects constitute the ideal vehicle for applying and acquiring chemical engineering knowledge in all its forms. Indeed, accreditation bodies such as ABET (USA) and IChemE (on behalf of the Engineering Council, UK) view the quality of senior design projects as a sort of health check of the programs that lead to an undergraduate degree. When properly researched by advising faculty members, senior design projects involving petrochemical processes can provide the complete ABET 2000 learning outcomes from a to k. Indeed, when the overall chemical engineering program learning outcomes show deficiencies in certain areas, a design project is often the balancing mechanism for bridging gaps in educational outcomes in the form of "integrating learning umbrellas."

From the author's long experience in supervising a wide range of senior design projects, the vinyl chloride monomer (VCM) process can be considered one of the most diverse, challenging, and complete design missions chemical engineering undergraduate student groups can engage in. Indeed, the VCM process history is well established, its safety and environmental impact attributes are well documented, and the diversity of process equipment associated with VCM plant operations is second to none.

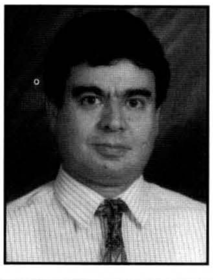
The VCM process is the subject of a case study in process synthesis in the latest edition of the textbook written by Sieder, *et al.*[1] In fact the VCM process is so "rich" in chemical engineering principles and plant operations that it can be offered to several groups of students in the same year with little or no overlap—or it can be offered to single groups every year, tweaking design objectives to make the successive years of student design work experience complementary and cumulative. This latter approach has been very powerful and generates useful educational data for faculty members interested in surveying collaborative and cooperative learning in major design assignments.

In this paper, the author shares his experience in supervising senior design projects in accredited chemical engineering departments (by the Institution of Chemical Engineers, UK and ABET, UAE) by providing full details on the VCM process, on the typical design tasks expected from groups of students, and on the wider learning outcomes that make such senior design projects fully compliant with ABET 2000. The details of the process described in this paper are based on extracts compiled from nonconfidential actual plant data supplied by the European Vinyl Corporation to assist process design at UK chemical engineering departments.

THE VCM PROCESS DESIGN BRIEF

Staged Learning Outcomes • The design groups comprised teams of 3 to 5 students. In the United Kingdom (Teesside University) the groups had mixed-ability students, according to GPA scores, and in the United Arab Emirates (UAE University), students were allowed to choose partners. The instructor acted as a client at the beginning of the project, but thereafter acted as a consultant where "penalty points" were incurred for excessive requests for help. The rule was clearly explained to students at the outset and did not pose any particular concern. Such a rule is primarily aimed at showing the degree of independence in the work achieved and is somewhat related to the final grade. This approach allows weaker groups to make progress at a "cost," does not give unfair disadvantage to more independent groups, and is considered fair by students themselves.

The design project was presented to the students as a for-



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mal "invitation for tender" from a "local" client in a suitably phrased letter. A "standard starter pack" consisting of initial references, essential design data or information not easily available in the library was also distributed to the student groups.[2-14] An extract of the content of this pack is presented in the sections below.

The student groups were either allocated names of fictitious contractor companies or allowed to name themselves as such. They responded to the invitation for tender by submitting a design proposal that included details of the approach to be adopted, milestones, and deliverables.

Students are exposed to a strong element of project management at the outset. The grading philosophy takes into account the following ABET learning outcomes that were staged (denoted by the letters shown in parenthesis):

- *Literature study: market, available technologies, safety/ environment, societal impact, process route selection (f, h, j)*
- *Acquisition or analysis of provided plant design data (b)*
- *PFD, material and energy balance of selected process after evaluating alternatives (a,c,d,e,k)*
- *PID and HAZOP study (d,e,f)*
- *Costing and project economic evaluation (h,k)*
- *Mechanical design of major items of equipment and application of suitable standards (c,d,e,k)*
- *Final report, poster, presentation, web site (d,g,k)*

DESCRIPTION OF THE PROCESS AGREED TO BETWEEN CLIENT AND CONTRACTOR

The process agreed to (after a thorough literature review and technical evaluation of alternatives) is based on the "balanced" VCM process. It comprises 3 reaction sections, a purification section for the intermediate 1,2-Dichloroethane (EDC), and a purification section for VCM. Process information and data from real plants, compiled in a condensed form,[2] are made available to students along with a list of start-up references.[3-14] The substance and structure of information supplied to students were designed to encourage cooperative work and critical thinking. This is presented in the following sections and constitutes a sizeable amount of the undergraduate design experience described in this paper.

TABLE 1
Extent of Side-Product Formation

$FeCl_3$ in EDC (g/m^3 as Fe)	*Oxygen in feed (% v/v in Cl_2)*	*Temperature (C)*	*B-tri formed (ppm w/w)*
50	0.5	60	2000
2000	0.5	60	1500
50	2.5	60	500
2000	2.5	60	400
50	0.5	84	50000
2000	0.5	84	5000
50	2.5	84	10000
2000	2.5	84	2000

DIRECT CHLORINATION SECTION

Process Chemistry • The reaction between gaseous ethylene and gaseous chlorine to form EDC takes place readily in a liquid EDC phase at moderate temperature and is strongly exothermic. The further chlorination of EDC to beta-tricholoroethane, or B-tri, (substitution reaction) takes place to a limited extent. The substitution reaction is inhibited by the presence of iron (in the form of $FeCl_3$) and dissolved oxygen. The effect of these inhibitors is additive. The degree of substitution is also temperature-dependent. These relationships (shown in Table 1) constitute a subject for discussion among the students.

As can be deduced from Table 1, there are two possible processes: 1) the "sub-cooled process" at 60°C where EDC is maintained below boiling temperature by circulation through an external cooler, and 2) the "boiling process" where the reactor contents are maintained at boiling by allowing vapor to boil off and condense externally, with some of it being returned to maintain the liquid inventory. The sub-cooled process produces a purer organic product but is iron contaminated, while the boiling process gives more B-tri but can in principle be obtained iron free.

The material fed to the cracking furnace is

B-tri	500 ppm w/w
Fe	1 ppm w/w

Process Details • The reaction of ethylene and chlorine proceeds very rapidly. The rate-limiting factor is believed to be the dissolution of ethylene in EDC. Therefore the reactor, whether sub-cooled or boiling, should be designed to provide adequate residence time for the gas dissolution, to avoid excessive liquid carry-over in the vapor stream leaving the reactor, and for proper sparging of the feed gases into the reactor. Actual production data suggests that a production of 500 kg/h EDC per m^3 hold-up of liquid can be achieved. In addition, sparging velocities of around 100 m/sec are appropriate.

To ensure complete reaction of the chlorine, it is normal to work with a slight ethylene excess in the ratio of gases fed to the reactor. The excess ethylene should be of the order 0.5 - 1.0 % by volume compared to chlorine. The presence of oxygen in the chlorine feed, together with other flammables that are present, gives rise to a potential flammability hazard in the final vent from the direct chlorination reactor and must be prepared for in some way.

If a sub-cooled reactor is chosen, the EDC product must be

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washed to remove iron chloride. This is preferably done in two stages—the first stage using water and the second stage using dilute caustic soda. In each case, the volume of aqueous and organic phases continuously in contact should be approximately equal. The wet EDC must then be dried by azeotropic distillation.

If a boiling reactor is chosen, there is no need to wash the bulk of the product (providing precautions are taken against liquid entrainment), and therefore no drying is required. There will still be a need to periodically wash the purge stream, however, when the solids content becomes too high. This is normally done by pumping out the vessel contents batch-wise to a wash system and replenishing it with a fresh catalyst charge. This should be done when the ratio of EDC made to vessel contents exceeds, say, 200. As stated before, boiling reactor material will have to be processed through a distillation column to remove B-tri.

Vent gases can be released into the atmosphere providing the total emission of chlorinated hydrocarbons is less than 10 kg/h, but precautions must be taken against a breakthrough of chlorine due to loss of ethylene feed or any other reason. It is normal to provide a large scrubbing tower that has a caustic soda solution permanently recycled through it and is capable of neutralizing the full flowsheet rate of chlorine.

Feedstocks • Ethylene is available at 100 psig (690 kPa) pressure and ambient temperature. It will contain up to 400 ppm by volume of ethane.

Chlorine is available either as cell gas or as revaporized liquid. Both can be made available at 30 psig (207 kPa). Cell gas will contain the following impurities:

Oxygen	*2% v/v*
Nitrogen	*0.5% v/v*
Hydrogen	*0.1% v/v*
CO_2	*0.15% v/v*

Revaporized liquid chlorine can be assumed 100% pure.

CRACKING SECTION

Process Chemistry • EDC pyrolysis is an endothermic reaction and is normally carried out as a homogeneous non-catalytic gas-phase reaction at elevated temperature and pressure in a direct-fired furnace. Free-radical chain reactions are involved with chlorine atoms acting as the chain propagators. The product of the main reaction, vinyl chloride (VC), is itself highly reactive towards free radicals. This gives rise to a significant group of by-products that includes acetylene, chloroprene, and dichlorobutenes.

The quantity of by-products formed per ton of VC made increases rapidly as the fractional conversion of EDC per pass ("depth of cracking") increases (see Table 2).

Other factors such as the pressure, the level of impurities (especially iron) in the EDC feed, the residence time of gases in the cracking reactor, and the tube wall material used in that reactor, all have some bearing on the by-product spectrum but it can be assumed that the depth of cracking is the dominating parameter.

One by-product in the EDC feed, beta-trichloroethane, will partially undergo pyrolysis to vinylidene chloride. Empirical data indicates that the ratio of B-tri converted to EDC is roughly 0.4.

As can be deduced from Table 2, a low depth of cracking is desirable to minimize by-product formation. A low crack, however, implies increased steam use in the distillation columns used to separate the cracked gases and to further purify the uncracked EDC before it can be recycled to the cracking furnace. An optimum depth of crack is thus sought.

In addition to volatile by-products, tarry and carbonaceous materials are formed in the cracker. They deposit inside the reactor tubes and eventually cause reduced heat transfer and increased pressure drop to such an extent that the reactor must be shut down for "decoking." Real plant data shows that (not surprising) the fouling is also a strong function of depth of crack—this can be seen in Table 3.

Each decoke causes a shutdown of the reactor for about 72 hours. Fixed costs for the plant are $400/hour.

Process details • Purified EDC is stored as a liquid at ambient temperature in an atmospheric-pressure storage tank. It has to be pumped up to pressure, vaporized, and passed into the cracking furnace. The cracked gases are quenched by a recirculation stream of liquid EDC to terminate the cracking reaction, and then they pass through one or more con-

TABLE 2
Impurities Formed ppm w/w of VC Product

	45% Crack	*50% Crack*	*55% Crack*	*60% Crack*
Acetylene (C_2H_2)	1000	1600	2500	4000
Chloroprene (C_4H_5Cl)	2000	3000	4500	7500
Dichlorobutenes ($C_4H_6Cl_2$)	3000	4500	7000	12000

densers to partially condense the products.

The mixture is then separated into three constituents—HCl, VC, and EDC. It is conventional to remove the HCl as the overhead product from a first column and then to separate the VC and EDC in a second column. The HCl overhead product can be taken off as a vapor, but there is still the need of a refrigerated condenser to provide reflux for the column. Economics require that the VC column condenser avoid refrigeration.

A key parameter to select is the operating pressure. EDC has to be vaporized at the front end of the process at one pressure and HCl condensed at some lower pressure at the back end, allowing for the pressure drop through the process train. To help determine the appropriate pressure we need to bear in mind that

1. The minimum pressure at the top of the HCl column should be 100 psig (690 kPa) to enable HCl to pass to the oxychlorination section without compression.
2. The maximum temperature at which it is advisable to vaporize EDC is about 220 C because above this it tends to thermally degrade and cause fouling of heat transfer surfaces.
3. We must allow a reasonable pressure drop through the cracking furnace, especially when fouled. Minimum values are typically 20 psig (138 kPa) clean, 35 psig (241 kPa) fouled and we would allow 1/4" (0.635 cm) coke layer formation inside the cracker tube wall before decoking.
4. In the refrigeration machine for the HCl condenser we would consider using an environmentally friendly fluorocarbon refrigerant as the working fluid, making sure that we do not go much below atmospheric pressure in the boiling refrigerant on the service side of the HCl condenser. This is to avoid having to handle very large volumes of gas into the suction of the refrigeration compressor and also to avoid air ingress into the machine.

Other Design Parameters • Maximum radiant heat flux to cracker furnace tubes: 12000 Btu/hr.ft^2 (37.85 kW/m^2). Maximum inside tube wall temperature for stainless steel grade 321: 570 C. Number of parallel tube passes in furnace: 1 or 2 (more makes control difficult).

Table 4 shows the equivalence of residence time and cracker exit temperature to give the same VC output at same depth of crack.

Feedstocks and Products • EDC fed to the cracker should have a minimum purity of 99% by weight. Specific impurity maxima are shown in Table 5.

TABLE 3
Depth of Crack and Run Life

Average Depth of Crack (%)	*Average Run Life (days)*
45	300
50	250
55	180
60	100

TABLE 4
Residence Time and Cracker Exit Temperature

Mean Residence Time of Gases in Radiant Section (calculated on exit conditions) (sec)	*Exit Gas (C)*
5	525
9	500
16	475

TABLE 5
Impurity Maxima for Cracking Section

C1 lights	2000 ppm w/w
C2 lights	4000 ppm w/w
C4 lights	100 ppm w/w
C2 heavies	1000 ppm w/w
C4 heavies	50 ppm w/w

Definition of lights and heavies:

C1 lights:	($CHCl_3$ + CCl_4)
C2 lights:	(C_2H_5Cl, $C_2H_2Cl_2$, C_2HCl_3, C_2H_2)
C2 heavies:	($C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2Cl_4)
C4 lights:	(C_4H_5Cl)
C4 heavies:	($C_4H_6Cl_2$)

The final vinyl chloride (VC) product produced should not contain more than 100 ppm by weight total impurities.

HCl and EDC separated from the cracked gas mixture should each not contain more than 200 ppm by weight of VC.

OXYCHLORINATION SECTION

Process Chemistry • The oxychlorination of ethylene by HCl and oxygen is catalyzed by copper chloride, normally supported on alumina. In addition, a direct oxidation of ethylene to CO_2 occurs. Normally, oxychlorination is the dominant mechanism and the oxidation reaction accounts for only a few percent of the ethylene converted. Catalyst activity increases with temperature but an increased temperature favors oxidation at the expense of oxychlorination. There is thus an optimum temperature, and the acceptable operating temperature range in the reactor is small. This factor, combined with the high exothermicity of the reaction, has led to the use of fluidized-bed catalytic reactors for large-scale operations. For fluidized-bed operations, a mean catalyst particle size of about 100 microns can be assumed. The particle size distribution can also be assumed if it is not available in the literature. In the absence of contact-time data for fluidized-bed operations, data for fixed-bed reactors can be used.

Some processes do employ multitubular fixed beds, however. Comments on drawbacks of fixed-bed reactor technology for highly exothermic systems are encouraged.

Experimental data obtained with a certain catalyst formulation is shown in Table 6, next page, (on a once-through, *i.e.,* no-recycle basis). In addition to the main oxychlorination reaction to produce EDC, there are other chlorinated hydrocarbons formed. On analysis, an approximate composition of the dry organic product is found to be

C1 lights ($CHCl_3$ + CCl_4)
8000 ppm w/w
C2 lights (C_2H_5Cl, $C_2H_2Cl_2$, C_2HCl_3)
5000 ppm w/w

C2 heavies ($C_2H_3Cl_3$, $C_2H_2Cl_4$, C_2Cl_4)	12000 ppm w/w
Balance EDC	

It can be assumed that any acetylene and VC brought in with the HCl is directly oxidized.

Process Details • A major decision to be taken concerns the construction material used for the reactor shell and cooler bundle. Obviously, the gas mixture has to be kept above the dew point or very rapid corrosion will ensue, but industrial data shows that the onset of corrosion occurs at temperatures well above the theoretically calculated dew point. This is due to complex erosion/corrosion mechanisms that are not well understood. There is also an upper temperature threshold above which corrosion increases, but the effect is not so clear-cut as the lower limit.

The key parameter to be studied in a metallurgical analysis is the partial pressure of steam in the reactor product gas mixture because this has a prime influence on the dew point. Table 7 shows recorded data.

The reactor must contain means of properly introducing the main feeds, bearing in mind that ethylene and oxygen (or air) should not be premixed outside the reactor. Facilities to remove most of the catalyst particles entrained in the reactor exit gases are also needed.

Upon leaving the reactor, the gases have to be quenched and condensed, and residual HCl must be neutralized. The organic and aqueous phases are separated, with the former being sent to an azeotropic drying column and the latter to a stripping column to recover dissolved EDC.

If an air fed process is chosen, the vent gasses leaving the main oxy condenser must pass through equipment to recover as much EDC as practical before being vented. If an oxygen process is chosen, most of the gas will be recycled to the reactor to achieve the desired gas partial pressures, and only a small amount is vented to maintain pressure control.

Feedstocks and Products • The compositions of ethylene and HCl were given earlier in this paper. Oxygen purity is not critical and will normally be supplied as 99% by volume at whatever pressure required. The EDC product purity was also given. The aqueous effluent should be steam stripped to give less than 5 ppm EDC by weight in the final effluent discharge. Assume that the vent gas hydrocarbon content does not exceed 10 kg/hour.

Plant Operation Data

- Plant attainment: 94%
- Annual production of VCM: 150 000 000 kg

Cost and Economic Data

- Average market price for VCM (over period 2000-03): \$700/1000 kg
- Average market prices for Ethylene, Oxygen ,and Chlorine (over 2000-03) are 360, 45, and 150 US Dollars per metric ton, respectively.
- Expected plant life: 25 years
- Capital: To be estimated from step-counting method[8] in US dollars; prices must be adjusted for inflation using the cost index in the United States. The total investment can be distributed as follows:
  - *Year 1* - Design costs: 9% of capital cost
  - *Year 2* - Construction phase 1 costs: 45.45% of capital cost
  - *Year 3* - Construction phase 2 costs: 45.45% of capital cost
  - *Year 4* - Working capital: 13.60% of capital cost
- Fixed operating costs were estimated to be
  - 3.7% of the capital cost per year, up to year 10
  - 4.6% of the capital cost per year after year 10, up to year 17
  - 5% of the capital cost per year from year 17 onward
- The variable operating costs were estimated to be
  - \$15 per ton (1 ton = 1000 kg) of product up to year 17
  - \$18 per ton of product from year 17

TYPICAL DESIGN TASKS

In the structured report, the student is instructed to

- Write a cover letter to your client when you hand in your design report.

TABLE 6
Oxychlorination Kinetic Information

Conversions at contact time of 15 sec	*Operating temperature (C)*			
	230	*240*	*250*	*260*
% HCl converted	95	97	98.5	97.5
% C_2H_4 to EDC	93	95	95	93
% C_2H_4 to CO_2	2	2.5	3.5	5
% C_2H_4 converted	5	2.5	1.5	2

Conversions at operating temperature of 250 C	*Contact time (sec)*		
	10	*15*	*20*
% HCl converted	96	98.5	97.5
% total C_2H_4 converted	95.5	98.5	98.5
% total O_2 converted	90	96	98

TABLE 7
Water Partial Pressures and Corresponding Acceptable Temperature Ranges

Metal	*pp H_2O (bar abs)*	*Acceptable Temp. Range (C)*
Mild steel	1	200-260
	1.5	None
Stainless steel 316	1	190-300
	1.5	210-300
	2	None
Iconel	1	160-280
	1.5	190-280
	2	220-280
Hastelloy	1	160-300
	1.5	170-300
	2	180-300

- Write an introduction section that provides information about VCM, its applications and safety issues, the world market situation, and a balanced societal impact (benefits and potential problems).
- Select a suitable site (in the country of residence of students during their studies) to locate the VCM plant. Justify your site selection and carry out an environmental impact assessment, using accident or accidental spill/release scenarios.
- Produce the complete PFD for the process described above. Use a computer drawing tool.
- Carry out a complete material balance using the spreadsheet presentation method. You may find it convenient to divide the process into smaller sections when reporting the material balance tables with portions of the PFD in the spreadsheet.
- Carry out a complete energy balance, stating clearly any assumptions made. You may also employ HYSYS for part of the energy balance calculations where there is a justification for doing so.
- Produce a complete PID for the **oxychlorination section** justifying all instruments implemented.
- Carry out a detailed HAZOP analysis on 4 streams in the oxychlorination section using keywords: NO, LESS, MORE on deviation FLOW. You must refer to the PID symbols produced before in the HAZOP table. Adjust your PID in the light of recommendations from your HAZOP study.
- Carry out a detailed mechanical design of the oxychlorination reactor and its ancillary equipment. State and justify any assumptions made, and refer to appropriate design standards.
- Carry out the following economic analysis of the process:
  - The net cash flow in each year of the project and plant operation
  - The future worth of the project, NFW
  - The present worth, NPW, at a discount rate of 15%
  - The discounted cash flow rate of return, DCFRR. Explore discount rates 25%, 35% and 40% to tabulate values, but use Excel Solver for the final answer. Produce a suitably labeled cash flow diagram too.
  - Estimate the pay back time.

ALTERNATIVE DESIGN TASKS

Different annual production rates may be given to different groups or in successive years, according to situations in departments (*e.g.,* do students readily have access to past design reports? Are students monitored and quizzed periodically for original contribution? etc.). Mechanical design of different major items (there are a few in the VCM process and most are challenging) for each group or in successive years (direct chlorination reactor, cracking furnace, distillation columns, etc). Depending on whether simulation tools are allowed, the level of design complexity can be adjusted accordingly. The process economic evaluation can be made more complicated by assuming variable raw material costs over the plant lifetime. HAZOP and operability studies can also be made more challenging—that would be an ideal exercise for team cooperative work. The same approach can be adopted for process instrumentation and control.

CONCLUSION

The VCM process design project has been offered to a multitude of groups of international students in the UK and UAE for a period spanning ten years and was found to be an excellent vehicle for integrating scientific knowledge, chemical engineering principles, and a whole range of transferable and interpersonal skills, thus making it a truly ABET 2000 compliant senior-design project. The way design information has been provided to students enables them to engage in critical thinking and to evaluate constrained alternatives. On completion of the demanding design tasks, virtually all students recognized the benefits of working on such projects. The faculty member advising the students also benefited from the experience of supervising such project and became in a stronger position to revise curricula and propose relevant changes where appropriate. Details of the VCM process presented in this paper are based on real plant data that are believed not to be available anywhere else, thus making this article of major benefit to faculty members and students alike.

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